

ELECTRICAL SPECTRA OF METALS.

RESULTS OF AN EXAMINATION AS TO THE PRACTICABILITY OF ASSAYING METALS USED IN COINAGE, BY MEANS OF SPECTRUM ANALYSIS, MADE IN AND FOR THE ASSAY DEPARTMENT OF THE U. S. MINT AT PHILADELPHIA.

BY ALEX. E. OUTERBRIDGE, JR.

Communicated to the American Philosophical Society, by MR. W. E. DU BOIS, Assayer of the Mint, May 15th, 1874.

It must have occurred to many, when this brilliant method of scientific research succeeded in detecting the presence of metals, in any given substance, even to an infinitesimal nicety, that the next step must be to determine the *proportion* of such presence; in other words, the *qualitative* must certainly lead to the *quantitative*, as in other chemical processes.

The Annual Report of the Royal Mint at London, for 1872, (dated 15th of April, 1873,) contains an official memorandum of Mr. W. Chandler Roberts, Chemist of the Mint, from which it appears that he was engaged in examining this subject, at the suggestion of, and in connection with, the distinguished spectroscopist and astronomer, Mr. J. Norman Lockyer. No decided results had been reached; but Mr. Roberts concluded by expressing the belief "that every effort should be made to render the instrument serviceable in the operations of minting."

The present modes of assaying gold and silver, both in alloys and in ores, have been brought to such perfection, such accuracy, delicacy and dispatch, that it seemed almost a matter of regret to have them superseded or disturbed. And yet, there is something captivating in the idea of a determination, as it were by a flash of lightning, or in the twinkling of an eye, what proportion of gold or silver is present, in any bar, or coin, or native ore. It therefore seemed desirable that our own Mint should maintain its character for examining and adopting real improvements, and not to wait indolently to hear what might be done abroad.

One of the assistants in the Assay Department, Mr. Alexander E. Outerbridge, Jr., had for several years given special attention to spectroscopic studies, both in theory and in practice; and to him therefore, the subject was committed; with what propriety, and what success, will sufficiently appear from what he has written. This will be found in the two following communications addressed to the Assayer.

The details he has given are well worth a careful study; but we cannot help noticing, in a few words, the astonishing paradox at which his experiments arrive; namely, that this method is, in one respect, by far too sensitive and minute; and in another respect, far from being minute enough, to serve the uses of assay. It was worth all his patient labor many times over, to come to this conclusion; as we must come in the present state of this branch of science. And it is likely, that the natural and necessary imperfections of metallurgy, the want of complete atomic homogeneity in the mixing of metals, will forever prevent the spectro-scope from taking the place of the present methods of assay.

As Mr. Outerbridge has been careful to give facts rather than suppo-

sitions, he has omitted any explanation of the anomalous results in the final part of his report. And yet it seems evident that where two metals are present, the spark will to some extent elect for its vehicle the one which is most rapidly vaporized. This is notably shown in alloys of gold with copper. It is also very striking in the alloy of nickel and copper, of which our five-cent piece is made. The nickel, which constitutes one-fourth, controls the color of the alloy entirely; and yet, being far more difficult of fusion than the copper, scarcely shows a trace in spectrum analysis. This result is particularly regretted, because a shorter way of assaying this mixture for coinage is very desirable.

These experiments, it is believed, will be of use to show what may, and what may not, be expected from the spectroscope in the way of analysis where several metals are components. They may also be of use in other departments of investigation.

D.

Philadelphia, October 30, 1873.

WM. E. DU BOIS, ESQ.,

Assayer U. S. Mint.

SIR :—In pursuance of instructions received from you, to examine the subject of the “Electrical Spectra of Metals” with a view to its possible application to assaying, I beg respectfully to report, as follows :

With a small induction coil, and with a two-prism Browning Spectroscope, I tried some experiments to obtain the effects recently discovered by Mr. J. Norman Lockyer, of England, viz., the discernment of differences in the lines of the Spectra of different Alloys of Gold and Silver. In other words, to utilize the Spectroscope as a means of *quantitative*, as well as of *qualitative* analysis.

I had several interviews with Professor Barker, of the University of Pennsylvania, (a recognized authority on the Spectroscope), who had recently met Mr. Lockyer in England, and to whom I am indebted for valuable information pertaining to the subject.

I soon found that although I was able to distinguish clearly between the spectra of pure gold, 1000 fine, and of an alloy of gold and copper 900 fine, inasmuch as the copper lines appeared in the one case, and not in the other, the induction coil was quite inadequate in its length of spark to exhibit any appreciable differences between two alloys of gold and copper. I then applied for, and was accorded by my friend President Morton, of the Stevens Institute of Technology at Hoboken, the privilege of conducting my experiments at that Institution.

Professor Morton most kindly placed at my service the elaborate apparatus in his collection; and I visited New York on Monday last, the 27th inst., returning this evening.

During these four days, I experimented very critically with known alloys of gold, silver and copper, previously prepared for this purpose, and I obtained some very interesting results. Many practical difficulties

presented themselves in the outset, and it was some time before I succeeded in obtaining a special adjustment of the apparatus appropriate to my purpose.

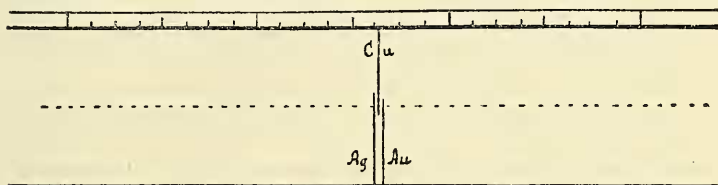
Using one-half of the largest Ritchie induction coil, throwing a spark of eleven inches, (fed by a powerful battery and reinforced by four large condensers) in connection with a two-prism Browning Spectroscope, I found that upon gradually separating the metallic electrodes, certain of the lines *broke in the middle*; and, upon further increasing the distance between the electrodes, the hiatuses in the spectral lines increased proportionately, *but unequally with different alloys*.

This, as I am informed, is the novelty in spectroscopic research, discovered by Mr. Lockyer, upon which the theory of possible quantitative analysis is founded, and I was much gratified at having verified the experiment.

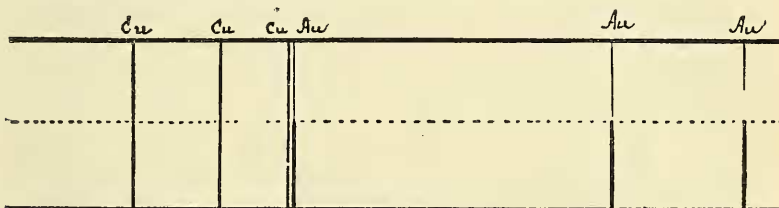
Repeated trials with various alloys, gave similar effects. Having proved this general incident, a systematic series of experiments with alloys enabled me to map the difference of fineness between specimens 500 and 750 fine and even to recognize the variation between ingot-slips 895 and 902 fine. These results were observed by Mr. Andrew Mason, of the New York Assay Office, and by several members of the National Academy of Sciences, then on a visit to the Stevens Institute, as also by other gentlemen, to whom some of the experiments were shown. The variation within seven thousandths above referred to, was by no means marked—indeed, over-cautiousness prevents my relying upon its certainty—although a more delicate adjustment of apparatus and further experience would probably render the distinction more decided. Of course, in these experiments, it was necessary to eliminate the numerous air lines which appeared in all the spectra. A difficulty which presented itself in the exact comparison of certain characteristic lines of gold, silver and copper, whose positions in the spectrum are in close proximity, was overcome by using a pure metal as one electrode and another pure metal as the other electrode. The effect thereby produced was very curious. With pure gold and pure copper as the electrodes, the gold lines extend across only one-half the field of the spectrum, and the copper lines extend across only the other half, the medial termini of both sets of lines being perfectly sharp and bright. By this means a double spectrum of copper and gold is obtained, or rather, a section of a complete gold spectrum and a section of a complete copper spectrum are visible in immediate juxtaposition, thereby enabling a most accurate comparison of lines, which in reality are not identical in position, but which by the previous method were apparently so.

By a slight modification of the experiment, substituting pure copper as one electrode and an alloy of silver and gold as the other, the proximate lines of these three metals are presented mapped, as it were, on a

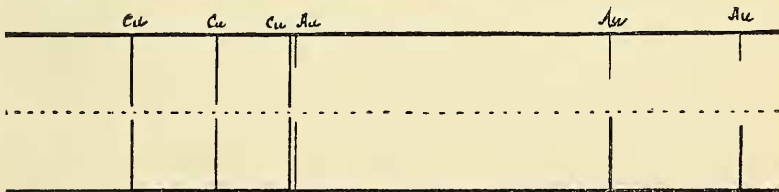
natural scale. Further modifications of this principle suggested themselves and were tried with indications of valuable results. (Fig. 1.)



By using as one electrode, an alloy of gold and copper of comparative fineness, and a baser alloy of the same metals as the other electrode, a result not before observed presented itself. The lines of both copper and gold crossed the entire field of vision, but in the section representing the fine alloy, the gold lines were strong and bright, while in the section representing the base alloy the gold lines were very faint. (Fig. 2.)



By now gradually increasing the distance between the electrodes, the faint gold lines of the base alloy cease to join their bright counterparts of the fine metal at the central line. (Fig. 3.)



The intervening space is at first minute, but as the electrodes are further separated, the ends of the faint lines gradually recede towards the outer edge of the spectrum until they finally disappear altogether. A scale was constructed of the distances at which the electrodes were withdrawn during the several trials, and careful notes were made, but time did not permit an elaboration of these experiments by accurately testing the results when alloys of approximate fineness formed the electrodes. I had wished to use a spectroscope of greater dispersive power, (in order to observe as many distinct lines as possible), and also to magnify the lines by projecting the spectrum through a lantern upon a screen.

The general principle was satisfactorily proved, however, that where two alloys of different grades are subjected to this treatment, the gold lines of the baser compound are noticeably the fainter of the two, and, what is more important, they may be reduced in length by separating the poles, until they disappear.

This points to the possibility of the future application of Spectrum Analysis to Assaying, at least as a test method. For, if an alloy of absolute known fineness were adopted as one electrode, and an ingot-slip assayed by the old process to an equal grade of fineness were inserted as the opposite electrode, in case the assay were correct, the gold lines in both sections of the spectrum should appear of equal brightness, and more especially, should begin to recede from the central line of the spectrum at the same moment, and should disappear at the same moment.

The spectra being inevitable natural effects of physical causes, a variation between two specimens of supposed equal fineness would, in theory, be necessarily indicated by the respective lines failing to correspond in their reciprocal action. To use the method as a means of original assay, it would be necessary, among other things, to construct scales of delicate measurement which, if possible at all, could only be done by a long course of laborious investigation.

The experiments of which the foregoing is a resumé, involved many matters of practical detail to which it is unnecessary to allude, and having been conducted at short notice and within the brief period of four days, they must be considered as simply preliminary.

Respectfully submitted,

ALEX. E. OUTERBRIDGE, Jr.

Philadelphia, May 5th, 1874.

WM. E. DU BOIS, Esq.,

Assayer U. S. Mint.

SIR :—Since submitting to you my report of the 30th of October last, I have continued at intervals the investigation of the “Electrical Spectra of Metals,” with a view to the practical application of the spectroscope to Mint assaying.

Having repeated and proved the correctness of the experiments previously recorded, using a three-prism spectroscope and an induction coil capable of throwing an eight inch spark, (kindly furnished me by Dr. R. E. Rogers of the Medical Department of the University of Penna.) I found it necessary to devise a special apparatus for manipulating the electrodes when under examination. This was made for me by Mr. Saml. James, the machinist in the Mint, and admirably fulfilled its object. A photograph and description of it are appended hereto. Its peculiarity consisted

in an automatic combination of accurately proportioned screws, acting in opposite directions, by which a single motion of the hand sufficed to cause the upper and lower electrodes to approach or recede from the central line of contact in an equal degree. The electrodes, which consisted of small strips of metal cut to a point, were held by a suitable arrangement on the outer circumference of two metallic rings insulated from each other, the upper one slotted to receive a series of twelve electrodes of varying *known* fineness, and revolving horizontally, so that each electrode might in turn be adjusted to face a single electrode of *unknown* fineness fixed on the lower ring. Its object was to admit of the electrodes being separated to any desired extent, while preserving the line of vision, through the spectroscope, directed to the centre of the spark. This is a point of much importance.

A systematic series of experiments was now commenced, in which the behavior of the more volatile metals was at first studied, viz: Lead, Zinc, Bismuth, Tin, Antimony, Cadmium, Mercury, Aluminium, &c. All these give more decided spectra than the less volatile precious metals, and some interesting results were noticed. Approximate illustrations of some of these spectra are appended.

Proceeding to the examination of gold alloys, and starting with base poles—making the lower pole 250 fine and the upper pole 500 fine—the gold lines from the upper half were both longer and brighter. Now substituting in place of the 250 pole one 700 fine, the lower half showed the brighter gold lines. Then, changing the 500 pole for one 800, the brightness of the gold line was again reversed. This alternating effect may be continued, decreasing in degree as the fineness of the poles approach more nearly together, until both poles are of the same fineness, when the lines will be equal in length and intensity.

These experiments proved satisfactorily that comparatively wide variations in the composition of gold alloys were discernible. I now had prepared at the Mint a series of graduated alloys of more approximate fineness, viz :

GOLD AND COPPER.

938.

917.

906.

888.3

883.5

876.5

GOLD, SILVER AND COPPER.

940.1

918.7

866.8

888.

884.1

883.

These alloys were carefully prepared and assayed closely.

With one electrode pure gold and the other 938 fine, the difference between the respective spectra was of course very marked, the copper lines appearing in the one and not in the other. Substituting for the pure gold the alloy 876.5, the difference was still very marked, for, although both gold and copper appeared in each, the copper lines were much brighter and somewhat longer in the baser alloy, while the gold lines were

brighter and longer in the finer. But on comparing the alloys 876.5 and 883.5, (reducing the variation to seven thousandths) I was both surprised and disappointed to find the visible difference of result but slightly appreciable. And the same with regard to the alloys 883.5 and 888.3, and the same with other alloys with equal or less comparative variation of fineness. A variation of one-thousandth, required an effort of the imagination as well as of the eye to detect any difference whatever. And, although I endeavored to map an apparent difference between alloys varying two-thousandths, it would certainly not have been a safe test on which to base an assay. Frequent repetitions with changes of adjustment were tried, the battery power varying from one to six Bunsen cells, in connection with Leyden-jars varying from one very small jar (improvised out of a test-tube) to fifty large jars, (representing a metallic superficies of many square feet) with variations of the distance of the electrodes apart, and with and without the use of a condensing lens, but all these failed to give closer results.

It is true, that these changes of conditions produced certain variations in the effects observed—as, for instance, it was noticed that an increase in the Leyden jar surface always lengthened the lines—the distance between the electrodes and all other conditions remaining the same—while a decrease in the condensing surface had an opposite effect. Thus, to take the extreme cases, with the single small Leyden jar above referred to, and one cell of battery, the lines broke when the electrodes were not more than $\frac{1}{16}$ of an inch apart, and disappeared entirely on separating the points $\frac{1}{8}$ of an inch.

With fifty Leyden jars and six cells of battery, it was found impossible to break the lines at all, even by removing the electrodes to the extreme limit of the spark, and in this case new lines also appeared.

Other variations occurred; such as a momentary irregularity in the length and brightness of the lines, under a strong battery power, owing to the unequal action of the spark;—a difference in the action of the gold lines dependent upon the nature of the alloy, silver tending to lengthen them more than an equal admixture of copper;—the length of the lines is also dependent upon the distance between the spark and the slit (when the latter is used without the intervening condensing lens);—moreover, the eye itself is liable to become confused by continued comparisons of very slight differences. The above and other modifications, so far from solving the problem of close work, rather indicated possible sources of error.

Another element of the process suggested itself to me as likely to render the results uncertain for the practical purpose of assaying, viz: whether the quantity of metal vaporized and giving the spectrum is not too infinitesimal to give safe results for a large melt. This would be affected by the least want of homogeneity in the metal. This is a serious consideration, and with the view partly to search for unknown sources of error and partly to ascertain generally the quantity of metal operated on

in a spectroscopic assay, (should that ever be possible) the following experiment was tried. Having weighed small electrodes, averaging 18 milligrammes each, with the greatest possible accuracy on the gold assay balance of the Mint, (which is sensitive to a twentieth of a milligramme, or even less,) and having arranged a spark register, I found that 1000 sparks might be passed between these poles, each spark showing the spectrum of the metal distinctly, and yet the loss in weight was too small to be made the base of calculation. Thus, a gold pole lost in weight after passing 1000 sparks, $\frac{1}{10000}$ of a grain; this gives for each spark $\frac{1}{1000000}$ of a grain of gold, producing a bright spectrum. I increased the number to 3000 sparks as the test. The loss of weight depends of course upon the electric volume, and in the experiments tabulated I endeavored to keep the latter constant. A slight deposit of the vaporized metal from the opposite pole takes place in fine division, but this is easily removed—in the case of copper and gold poles by dipping the gold for a moment in weak acid, or by gentle rubbing. The annexed tables (marked A and B) show that the loss in weight is marvellously small, averaging less than seven-tenths of a milligramme of gold for 3000 sparks. To give the amount for each spark, this must be divided by the number of sparks; thus, in round numbers an electrode loses $\frac{3}{10000}$ of a grain after passing 3000 sparks; or for 1000 sparks $\frac{1}{10000}$ of a grain, or for each spark $\frac{1}{1000000}$ of a grain. The exceedingly small quantity of metal thus assayed renders this process, to my mind, inapplicable to the operations in the Mint; for it is necessary to determine gold assays to the $\frac{1}{10000}$ part of the normal assay weight, and it is hardly conceivable that a discrimination to the $\frac{1}{1000000}$ part of the spark assay weight, or the $\frac{1}{10000000000}$ of a grain is practically possible. Even if it were, it would not be proper to assume that a test on such an atomic scale would correctly represent the value of a large deposit, or even of gold ingots. It would certainly not be in the case of silver, which segregates.

The table of loss shows another curious and unexpected result, viz. : that the loss in weight of the volatile metals very slightly exceeds and in some cases does not equal the loss of the less volatile metals. Thus, in three different experiments of 3000 sparks each, copper loses but .1 M. while gold loses .5 M. It must be remembered that in these experiments a much stronger spark was used than was necessary to show a visible spectrum. When reduced to a minimum, as was done in the case of the miniature Leyden jar, which still gave a distinct spectrum, the loss in weight after 3000 sparks, for silver, copper and tin, was absolutely inappreciable on the balance.

An unexplained anomaly was also noticed in relation to the sensitiveness of the spectroscope to the metals present in small quantity. Although Mr. Cappel has shown, by passing the spark through weak solutions of pure metals, that $\frac{1}{40000}$ of a milligramme of gold will show a spectrum, (it is even less than $\frac{1}{80000}$ of a M. according to an experiment performed by the method described above) yet a comparatively large proportion of

gold may be present in an *alloy*, the presence of which will not be indicated at all by the spectroscope.

In a slip composed thus :	{	Silver, 708 parts.
		Copper, 254 "
the spectra of silver and copper are alone visible.		Gold, 38 "
		1000

In fact, in an alloy of gold and copper containing from 200 to 250 parts of gold, the gold spectrum is barely visible. In the case of gold containing copper, it was found that one per cent. of the latter sufficed to show the copper spectrum; likewise in an alloy of nickel and copper containing 20 per cent. of nickel, its spectrum is not visible.

If the spectroscope fails to reveal the presence of anything less than 200 parts of gold in a base alloy, even a theorist must admit that one could scarcely expect to be able to discriminate with certainty a variation of $\frac{1}{10000}$ in a fine alloy.

It is not impossible that future discovery may succeed in explaining this anomaly, in harmonizing the apparent inconsistencies, in eliminating the sources of error, and in reducing the operation to practicable certainty, but in the state of spectroscopic science as it now exists, so far as I have been able to perceive, I have arrived at the opinion, not without regret, that assaying by means of spectrum analysis is impracticable for the purpose of Mint operations.

In conclusion, it should be stated that the principal part of my work was performed at the University of Pennsylvania, with the benefit of the excellent apparatus and appliances afforded in the new and magnificent college building. For this privilege, and also for many valuable suggestions and for personal favors, I desire to acknowledge my indebtedness to Professor Geo. F. Barker of that Institution.

Very respectfully, yours,

ALEX. E. OUTERBRIDGE, Jr.

TABLES.

First column shows the weight of the metallic-electrodes in milligrams before passing the sparks.

Second column shows the weight after passing 3000 sparks.

Third column shows *total* weight of metal volatilized (in fractions of a milligramme).

Fourth column shows the amount of metal volatilized by *each* spark (in fractions of a milligramme).

Fifty column shows the amount of metal volatilized by each spark in fractions of a grain troy.

A

		1	2	3	4	5
*Upper Pole.	Gold	16.6	15.9	.7	$\frac{1}{4286}$	$\frac{1}{277000}$
Lower “	“	16.7	16	.7	“	“
Upper “	Copper	18.5	18.4	.1	$\frac{1}{30000}$	$\frac{1}{1940000}$
Lower “	“	“	“	.1	“	“
Upper “	Gold Ingot,	24	23.4	.6	$\frac{1}{5000}$	$\frac{1}{324000}$
Lower “	“ “	“	“	“	“	“
Upper “	Tin	20	19.6	.4	$\frac{1}{7500}$	$\frac{1}{486000}$
Lower “	“	“	19.4	.6	$\frac{1}{5000}$	$\frac{1}{324000}$
Upper “	Silver	24.8	24.6	.2	$\frac{1}{15000}$	$\frac{1}{976000}$
Lower “	“	25.1	25.	.1	$\frac{1}{30000}$	$\frac{1}{1940000}$
Average.	Lead	91.6	90	1.6	$\frac{1}{1870}$	$\frac{1}{121000}$

B

Upper.	Gold	20.5	20	.5	$\frac{1}{6000}$	$\frac{1}{388000}$
Lower.	Copper	10	9.9	.1	$\frac{1}{30000}$	$\frac{1}{1940000}$
Upper.	Gold Ingot	21	20.4	.6	$\frac{1}{5000}$	$\frac{1}{324000}$
Lower.	Copper	20.2	20	.2	$\frac{1}{15000}$	$\frac{1}{976000}$
Upper.	Silver	6	5.8	.2	$\frac{1}{15000}$	“
Lower.	Tin	20	19.4	.6	$\frac{1}{5000}$	$\frac{1}{324000}$
†Upper.	Nickel	12	11.95	.05	$\frac{1}{60000}$	$\frac{1}{3880000}$
Lower.	“	12	11.9	.1	$\frac{1}{30000}$	$\frac{1}{1940000}$

*NOTE—The upper pole usually formed the positive electrode.

†NOTE—The *minimum* of metallic Nickel producing a spectrum according to Cappel's tables is $\frac{1}{800}$ of a milligramme.

DESCRIPTION OF FIGURES 1 AND 2.*

A is a cast-iron base supporting the brass stem C which has a thread cut upon its lower end in order that it may be raised or lowered in the base A and firmly held in position by the jam nut B.

Into the stem C, a secondary stem D is screwed; this may be raised or lowered in stem C by turning the hand-wheel GH.

Upon the upper end of the *secondary* stem D is fitted a cylinder composed of the metallic band FF and the insulating centre G. This cylinder is held in position by the collars on either side, and is kept from rotating by a pin passing through the upper collar and sliding in a slot in the *third* stem E.

Through the stem C and secondary stem D passes a third stem E of steel, having upon its upper end a cylinder similar to the one before described, except that it is slotted to receive twelve strips of metal, while the lower cylinder is slotted to receive one strip. This cylinder is free to turn upon the stem E, and is fixed at any point by the nut upon the end of the stem.

The stem E is prevented from turning by a pin sliding in a slot in the lower stem C.

The pitch of the screw upon the stem E, is twice that of the screw on the lower end of the secondary stem D. In turning the hand-wheel GH in either direction, the stem E with the upper cylinder, though moving over twice the distance of the lower cylinder, yet moves an equal distance from a *central point between the two cylinders*, because the lower cylinder in moving from the central point carries with it the upper cylinder. It is to overcome the distance lost that the pitch of the screw upon the stem E is doubled.

The lower portion of the secondary stem D is divided into 24 degrees. A movement of a degree separates the electrodes $\frac{1}{288}$ of an inch.

*NOTE—Fig. 2 is reproduced by Mr. Carbutt, of Philadelphia, from the original drawings according to a modification of the Woodbury Photo-relief process.

With Fig. 2 are given in this No. of the Proceedings, and by the same process, fac-similes of two sets of drawings of spectra of various alloys described in the above memoir.

FIG. 1.—SECTION OF INSTRUMENT USED BY MR. ALEXANDER E. OUTERBRIDGE, JR., IN HIS SPECTROSCOPIC ASSAYS OF METALS USED IN THE COINAGE OF THE MINT AT PHILADELPHIA.

